



(19)

Europäisches Patentamt  
European Patent Office  
Office européen des brevets



(11)

**EP 0 837 176 B1**

(12)

**EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention  
of the grant of the patent:  
18.07.2001 Bulletin 2001/29

(51) Int Cl.7: **D06M 15/263**, D06M 15/55,  
D06M 15/564, D06M 15/568,  
D06M 15/572, D06M 15/333,  
A47L 25/00, C09J 7/04

(21) Application number: **96116910.9**

(22) Date of filing: **21.10.1996**

(54) **Tack-rag**

STAUBBINDETUCH

TAMPON D'ESSUYAGE

(84) Designated Contracting States:  
**AT BE DE DK ES FR GB IE IT NL SE**

• **Briel, Werner**  
**89537 Giengen (DE)**

(43) Date of publication of application:  
**22.04.1998 Bulletin 1998/17**

(74) Representative:  
**Hansen, Bernd, Dr. Dipl.-Chem. et al**  
**Hoffmann Eitle,**  
**Patent- und Rechtsanwälte,**  
**Arabellastrasse 4**  
**81925 München (DE)**

(73) Proprietor: **Briel, Werner**  
**89537 Giengen (DE)**

(72) Inventors:  
• **Börschel, Volker, Dr.**  
**72076 Tübingen (DE)**  
• **Hanne, Manfred**  
**70839 Gerlingen (DE)**  
• **Haeufler, Hartmut**  
**71686 Remseck (DE)**  
• **Vogt, Hermann**  
**73734 Esslingen (DE)**

(56) References cited:  
**GB-A- 610 169**                      **GB-A- 1 507 406**  
**US-A- 3 208 093**                      **US-A- 3 682 690**  
**US-A- 4 413 080**                      **US-A- 4 448 839**

• **DATABASE WPI Section Ch, Week 8520 Derwent**  
**Publications Ltd., London, GB; Class A82, AN**  
**85-119709 XP002030130 & JP 60 060 172 A**  
**(TAKAMATSU YUSHI KK), 6 April 1985**

**EP 0 837 176 B1**

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

## Description

[0001] The present invention relates generally to tacky cloths suitable for the removal of dirt, dust and other particulate contaminants (hereinafter simply referred to as dirt) from various surfaces. In the automobile industry, such tacky cloths are commonly referred to as tack-rags.

[0002] The use of articles coated with "tacky" resins for dirt removal purposes is generally known. See, for example, US3682690 and US3754991. US3658578 specifically discloses a cloth coated or impregnated with a tacky, amorphous polypropylene.

[0003] Tack-rags are normally produced by dipping a cloth material in a solution or dispersion of a tacky resin, then allowing the liquid medium to evaporate. The resins generally utilized are water-insoluble in order to facilitate cleaning and further use. Eventually, however, the tack-rags wear out and must be thrown away.

[0004] In the automobile industry, the current trend of legislation is to classify these resin-containing tack-rags in the same disposal category as paint wastes, thereby requiring special and increasingly expensive handling and disposal procedures. An alternative to the present tack-rags, therefore, would be highly desirable.

[0005] Such an alternative has now been discovered.

## Summary of the Invention

[0006] In accordance with the present invention, a tack-rag is provided which comprises a cloth material impregnated with a tacky resin, characterized in that the tacky resin is a non-drying tacky resin comprising an oligomer or polymer which possesses

- (a) one or more non-ionic water-solubilizing groups;
- (b) one or more ionic groups which, when neutralized with a non-volatile neutralizing agent, are rendered water-solubilizing; or
- (c) combinations thereof,

in a water-solubilizing amount or in an amount sufficient to render the oligomer or polymer water-soluble upon neutralization of the ionic groups if present.

[0007] The tack-rags in accordance with the present invention have the advantage that, subsequent to use, they can be water-washed to substantially completely separate the resin and collected dirt from the cloth material.

[0008] In the case wherein the resin is water-soluble because it possesses a water-solubilizing amount of (a) one or more non-ionic water-solubilizing groups, (b1) one or more ionic groups which have been neutralized with a non-volatile neutralizing agent in order to render those ionic groups water-solubilizing or (c) combinations thereof, it is not necessary to utilize any additives such as tensides in the wash water to effect substantially complete separation of the resin from the cloth material.

[0009] In the case wherein the resin only requires neutralization of the ionic groups to be rendered water-soluble, the only needed additive to the wash water is a non-volatile neutralizing agent which becomes associated with the ionic groups of the resin in order to render the ionic groups water-solubilizing and the resin water-soluble. Again, therefore, no tensides and the like are needed to effect substantially complete separation of the resin from the cloth material.

[0010] The so-washed cloth material, if in sufficiently good shape, can be reimpregnated with the tacky resin and used again as a tack-rag, or can merely be used for normal cleaning purposes. If disposal of the cloth material is required, the cloth material being substantially free of resin can simply be disposed of as normal waste.

[0011] In addition, the resin dissolved in the wash water can readily be recycled by removal of the dirt, e.g., by filtration, then concentration of the resin solution. The concentrated resin solution can then be reused as such or combined with fresh resin solution for (re)impregnating the cloth material.

[0012] These and other features and advantages of the present invention will be more readily understood by those skilled in the art from a reading of the following detailed description.

## Detailed Description of the Preferred Embodiments

[0013] As indicated above, the tack-rags in accordance with the present invention comprise a cloth material impregnated with a tacky resin, characterized in that the tacky resin is a non-drying tacky resin comprising an oligomer or polymer which possesses

(a) one or more non-ionic hydrophilic water-solubilizing groups;

(b1) one or more ionic groups which have been neutralized with a non-volatile neutralizing agent, or

(b2) one or more groups which upon neutralization with a non-volatile neutralizing agent form ionic groups, or

(c) combinations thereof;

in an amount sufficient to render the oligomer or polymer water-soluble, upon neutralization of said groups (b2) if present.

[0014] The dependent claims are directed to preferred embodiments of the invention.

[0015] Any one of a number of natural and/or artificial cloth materials may be considered suitable for use with the present invention. These cloth materials are generally known to those skilled in the art and include, for example, woven, non-woven and knitted cloths of cotton, polyester, wool, acrylic, nylon, rayon, cellulose (papers) and viscose fibers, as well as natural and synthetic

leather. Especially preferred are cotton, staple rayon and mixtures thereof.

[0016] As suitable tacky resins may be mentioned those that are non-drying and either water-soluble or capable of being rendered water-soluble by neutralizing ionic groups with a non-volatile neutralizing agent.

[0017] By "non-drying" it is meant that the resin dries by physical evaporation of the solvents to form a film in which the resin molecules retain their original chemical form, i.e., essentially no chemical reaction occurs such as crosslinking with a curing agent or via autoxidation at temperatures of up to about 150°C. The resin, therefore, should retain its tacky character at temperatures of normal use.

[0018] Suitable non-ionic water-solubilizing groups are well-known to those skilled in the art and include, for example, polyoxyalkylene groups such as polyoxyethylene and polyoxypropylene groups, as well as other hydrophilic groups based upon polyvinyl alcohols, polymers of hydroxy (meth)acrylates and other hydroxyl groups-containing oligomers and polymers. Preferred among these for use with the present invention are the polyoxyalkylene groups and, especially, polyoxyethylene groups.

[0019] Suitable ionic groups which require neutralization in order to be water-solubilizing are once again well-known to those skilled in the art and include, for example, carboxyl (anionic) and amino (cationic) groups, which are preferred.

[0020] In order to be useful for the present invention, these ionic groups must be capable of being rendered water-solubilizing by neutralization with a non-volatile neutralizing agent. By "non-volatile" is it meant that the neutralizing agent, once associated with the ionic group, does not readily dissociate from it and evaporate on drying. In other words, the salt formed on neutralization remains part of the resin upon drying, which is considered important in order to provide solubility of the resin in the wash water without the necessity for using additional tensides.

[0021] Suitable non-volatile neutralizing agents for anionic groups include strong bases such as alkali metal hydroxides, as well as higher molecular weight polyoxyalkylene amines such as those commercially available under the trade designation "Jeffamine" from Texaco Chemical Company. Preferred for use with the present invention include the alkali metal hydroxides such as LiOH, NaOH and KOH.

[0022] Suitable non-volatile neutralizing agents for cationic groups include inorganic strong acids such as phosphoric acid and sulfuric acid, as well as organic acids such as fatty acids and citric acid. Preferred for use with the present invention is phosphoric acid.

[0023] If the resin possesses only ionic groups, the resin should have an acid number or amine number of at least 20, preferably in the range of 20 to 275, and especially in the range of 40 to 90, in order for the resin to be rendered water-soluble upon neutralization of the

ionic groups.

[0024] Of course, the resins may also comprise combinations of these various water-solubilizing groups. If such combinations are utilized, one skilled in the art can readily determine the required amount of each of such groups in order to render the resin water-soluble.

[0025] As specific examples of resins suitable for use with the present invention may be mentioned the following:

(i) non-ionic - the reaction product of a biuret isocyanate trimer with one hydroxyl equivalent of a polyester polyol and two hydroxyl equivalents of a polyethyleneglycol monomethyl ether, the reaction product of a lower molecular weight bisepoxide with an amine alcohol (diethanolamine) without neutralization of the amine groups;

(ii) anionic/combination - acrylic resins containing acrylic acid and/or polyester and alkyd resins based upon polyols, polycarboxylic acids and monocarboxylic acids, the resins having an acid value of 20-275 (preferably 40-90) and a calculated molecular weight in the range of 800-8000 (preferably 1000-3000), with the anionic groups preferably being neutralized with alkali metal hydroxides as mentioned above; and

(iii) cationic/combination - resins based upon the reaction product of polyepoxide resins (such as the Epikote series commercially available from Shell) or glycidyl group-containing acrylic resins, with primary or secondary amines such as monoethanolamine, diethanolamine, ethylene diamine and diethylamine, the resins having an amine value of 20-275 (preferably 40-90) and a calculated molecular weight in the range of 800-8000 (preferably 1000-3000), with the cationic groups preferably being neutralized with phosphoric acid as mentioned above.

[0026] The cloth material may be impregnated with the tacky resin in any normal manner such as, for example, by dipping the cloth material into a solution or dispersion of the tacky resin or spraying such solution onto the cloth material, then allowing the solvent to evaporate. Evaporation can be accelerated through drying at slightly elevated temperatures and/or via air convection.

[0027] As suitable solvents may be mentioned any one of a number of organic solvents such as, for example, butyl acetate, xylene, white spirits and mixtures of water and a water-miscible solvent such as butyl glycol, as well as water in the case that the tacky resins are water-soluble.

[0028] As just indicated, solutions or dispersions of the resins are utilized for impregnating the cloth material with the tacky resins. In order to impregnate the cloth materials with a desirable amount of the resin, a dipping procedure is generally used with a continuous roll of ma-

terial being passed through a bath of resin solution. The viscosity of the solution is adjusted such that, after passing through rollers to remove excess resin then drying at ca. 100°C for 5-10 minutes, the weight of the so-impregnated cloth material amounts to 180-220% of the original cloth material weight (80-120% by weight added resin based upon the original weight of the cloth material). This procedure is controlled by weighing samples of the cloth material before and after impregnation.

[0029] The so-impregnated cloth material is then suitable for use as a dirt collector in various fields, but is especially suited for use as a tack-rag in the automotive field.

[0030] The tack-rags impregnated with a water-soluble non-drying tacky resin as described above can be readily cleaned by washing in water without the addition of tensides or the like which might create disposal problems with respect to the wash water. By so-washing the tack-rags, the resin and dirt can readily be substantially completely separated from the cloth material.

[0031] The tack-rags impregnated with a non-water-soluble non-drying tacky resin as described above can be washed in the same manner as those impregnated with a water-soluble resin with the exception that the wash water must contain a sufficient amount of a non-volatile neutralizing agent in order to neutralize a water-solubilizing amount of ionic groups present in such resin. Again by so-washing, the resin and dirt can readily be substantially completely separated from the cloth material.

[0032] The so-washed cloth material, if in sufficiently good shape, can be reimpregnated with the tacky resin and used again as a tack-rag, or can merely be used for normal cleaning purposes. If disposal of the cloth material is required, the cloth material being substantially free of resin and dirt can simply be disposed of as normal waste.

[0033] In addition, the resin dissolved in the wash water can readily be recycled by removal of the dirt, e.g., by filtration, then concentration of the resin solution. The concentrated resin solution can then be reused as such or combined with fresh resin solution for (re)impregnating the cloth material.

[0034] The foregoing more general discussion of the present invention will be further illustrated by the following specific examples.

#### Examples

##### Resin Solution 1

[0035] A non-drying alkyd resin (from unsaturated branched fatty acids, dicarboxylic acids and polyols), having a molecular weight of 1480 and an acid value of 68, was thinned with a 70/30 butyl acetate/butyl glycol solution to a solid content of 60 wt% and subsequently neutralized to 70% with a 40 wt% solution of sodium hydroxide in water.

[0036] This solution was further thinned with butyl acetate to a viscosity of 50 seconds (DIN 4mm cup, 23°C).

##### Resin Solution 2

[0037] The same as Resin Solution 1 except that the alkyd resin was neutralized to 100% with a 40 wt% solution of lithium hydroxide in water.

[0038] This solution was further thinned with butyl acetate to a viscosity of 50 seconds (DIN 4mm cup, 23°C).

##### Resin Solution 3

[0039] A polyurethane-modified polyester resin was prepared by reacting an hydroxyl group-containing polyester (acid value<3, MW=1230, from neopentylglycol, perhydrobisphenol and tetrahydrophthalic anhydride) with an adduct of one mole of a biuret isocyanate trimer (commercially available under the trade designation Desmodur N from Bayer AG) with two moles of polyethyleneglycol monomethyl ether. The resin was dissolved to 60 wt% in butyl acetate.

[0040] This solution was further thinned with butyl acetate to a viscosity of 50 seconds (DIN 4mm cup, 23°C).

##### Resin Solution 4

[0041] An epoxide-amine adduct from one mole of an epoxide resin (commercially available under the trade designation Epikote 828 from Shell) and two moles diethanolamine was thinned with butyl acetate to 60 wt%, then further thinned with butyl acetate to a viscosity of 50 seconds (DIN 4mm cup, 23°C).

##### Resin Solution 5

[0042] An epoxide-amine adduct from one mole of an epoxide resin (commercially available under the trade designation Epikote 1001 from Shell) and two moles diethanolamine was thinned with butyl acetate to 60 wt% then subsequently neutralized to 100% with phosphoric acid.

[0043] This solution was further thinned with butyl acetate to a viscosity of 50 seconds (DIN 4mm cup, 23°C).

##### Impregnation of Cloth Material

[0044] Cotton/rayon mixed cloth material was impregnated by dipping in the resin solution until, after drying at 100°C for 10 minutes, the cloth weighed about 200% of its original weight.

[0045] Tack-rags so-produced from each of Resin Solutions 1-5 had a tacky feel and exhibited excellent tack-rag properties, removing dirt from painted panels completely without smearing or leaving any residue on the painted surface.

[0046] These tack-rags were then washed in plain water without the addition of any tensides or the like (14

liters of water per kg tack-rag) and dried. The resulting rags were found to be completely tack free and suitable for general cleaning purposes.

#### Claims

1. A tack-rag comprising a cloth material impregnated with a tacky resin, characterized in that the tacky resin is a non-drying tacky resin comprising an oligomer or polymer which possesses

(a) one or more non-ionic hydrophilic water-solubilizing groups;

(b1) one or more ionic groups which have been neutralized with a non-volatile neutralizing agent, or

(b2) one or more groups which upon neutralization with a non-volatile neutralizing agent form ionic groups, or

(c) combinations thereof;

in an amount sufficient to render the oligomer or polymer water-soluble, upon neutralization of said groups (b2) if present.

2. The tack-rag according to claim 1, characterized in that the non-drying tacky resin possesses (a) one or more non-ionic water-solubilizing groups in an amount sufficient to render the oligomer or polymer water-soluble.
3. The tack-rag according to claim 1, characterized in that the non-drying tacky resin possesses (b1) one or more ionic groups which have been neutralized with a non-volatile neutralizing agent, in an amount sufficient to render the oligomer or polymer water-soluble.
4. The tack-rag according to claim 1, characterized in that the non-drying tacky resin possesses (b2) one or more groups which upon neutralization with a non-volatile neutralizing agent form ionic groups, in an amount sufficient to render the oligomer or polymer water-soluble.
5. The tack-rag according to any one of claims 1-4, characterized in that the ionic groups are anionic groups.
6. The tack-rag according to any one of claims 1-4, characterized in that the ionic groups are cationic groups.
7. The tack-rag according to any one of claims 1-6,

characterized in that the weight of the tack-rag is 180% to 220% of the weight of the cloth material.

8. A method of producing a tack-rag by impregnating a cloth material with a non-drying tacky resin as set forth in any one of claims 1-7.

9. A method of cleaning a tack-rag according to any one of claims 1 to 3 and 5 to 7 comprising a water-soluble oligomer or polymer as the non-drying tacky resin, characterized in that the tack-rag is washed in water, without the addition of tensides to substantially separate the resin from the cloth material.

10. A method of cleaning a tack-rag according to any one of claims 4 to 7 comprising a non-water-soluble oligomer or polymer as the non-drying tacky resin, characterized in that the tack-rag is washed in water without the addition of tensides to substantially separate the resin from the cloth material, wherein the wash water contains a non-volatile neutralizing agent in an amount sufficient to render the oligomer or polymer water-soluble upon neutralization of said groups (b2).

#### Revendications

1. Chiffon collant comprenant un matériau de tissu imprégné d'une résine adhésive, caractérisé en ce que la résine adhésive est une résine adhésive ne séchant pas comprenant un oligomère ou un polymère qui possède

(a) un ou plusieurs groupes de solubilisation dans l'eau hydrophiles non-ioniques ;

(b1) un ou plusieurs groupes ioniques qui ont été neutralisés avec un agent de neutralisation non volatil,

ou

(b2) un ou plusieurs groupes qui, sur neutralisation avec un agent de neutralisation non volatil, forment des groupes ioniques,

ou

(c) leurs combinaisons ;

en une quantité suffisante pour rendre l'oligomère ou le polymère soluble dans l'eau, sur neutralisation desdits groupes (b2) si présents.

2. Chiffon collant selon la revendication 1, caractérisé en ce que la résine adhésive non-séchante possède (a) un ou plusieurs groupes de solubilisation dans l'eau non-ioniques en une quantité suffisante pour rendre l'oligomère ou le polymère soluble dans l'eau.

3. Chiffon collant selon la revendication 1, caractérisé

en ce que la résine adhésive non-séchante possède (b1) un ou plusieurs groupes ioniques qui ont été neutralisés avec un agent de neutralisation non volatil en une quantité suffisante pour rendre l'oligomère ou le polymère soluble dans l'eau.

4. Chiffon collant selon la revendication 1, caractérisé en ce que la résine adhésive non-séchante possède (b2) un ou plusieurs groupes qui sur neutralisation avec un agent de neutralisation non volatil forment des groupes ioniques, en une quantité suffisante pour rendre l'oligomère ou le polymère soluble dans l'eau.

5. Chiffon collant selon l'une quelconque des revendications 1 à 4, caractérisé en ce que les groupes ioniques sont des groupes anioniques.

6. Chiffon collant selon l'une quelconque des revendications 1 à 4, caractérisé en ce que les groupes ioniques sont des groupes cationiques.

7. chiffon collant selon l'une quelconque des revendications 1 à 6, caractérisé en ce que le poids du chiffon collant est de 180 % à 220 % du poids du matériau de tissu.

8. Procédé de production d'un chiffon collant par imprégnation d'un matériau de tissu avec une résine adhésive non-séchante selon l'une quelconque des revendications 1 à 7.

9. Procédé de nettoyage d'un chiffon collant selon l'une quelconque des revendications 1 à 3 et 5 et 7 comprenant un oligomère ou un polymère soluble dans l'eau comme résine adhésive non-séchante, caractérisé en ce que le chiffon collant est lavé dans l'eau, sans l'ajout d'agents tensio-actifs pour séparer sensiblement la résine du matériau de tissu.

10. Procédé de nettoyage d'un chiffon collant selon l'une quelconque des revendications 4 à 7 comprenant un oligomère ou un polymère non soluble dans l'eau comme résine adhésive non-séchante, caractérisé en ce que le chiffon collant est lavé dans l'eau sans l'ajout d'agents tensio-actifs pour séparer sensiblement la résine du matériau de tissu, dans lequel l'eau de lavage contient un agent de neutralisation non volatil en une quantité suffisante pour rendre l'oligomère ou le polymère soluble dans l'eau sur neutralisation desdits groupes (b2).

#### Patentansprüche

1. Klebefreudiger Lumpen umfassend ein Gewebematerial, das mit einem klebefreudigen Harz imprägniert ist, dadurch gekennzeichnet, dass das klebe-

freudige Harz ein nicht trocknendes klebefreudiges Harz ist, umfassend ein Oligomer oder ein Polymer, das:

(a) ein oder mehrere nicht-ionische hydrophilsche wasserlösliche Gruppen,

(b1) ein oder mehrere ionische Gruppen, die mit einem nicht flüchtigen neutralisierenden Mittel neutralisiert worden sind, oder

(b2) ein oder mehrere Gruppen, die nach der Neutralisierung mit einem nicht flüchtigen neutralisierenden Mittel ionische Gruppen bilden, oder

(c) deren Kombinationen,

in einer Menge besitzt, die ausreicht um das Oligomer oder Polymer wasserlöslich zu machen, nach der Neutralisierung der Gruppen (b2), wenn vorhanden.

2. Klebelumpen nach Anspruch 1, dadurch gekennzeichnet, dass das nicht trocknende klebefreudige Harz (a) ein oder mehrere nicht-ionische wasserlöslich-machende Gruppen in einer Menge besitzt, die ausreicht, um das Oligomer oder Polymer wasserlöslich zu machen.

3. Klebelumpen nach Anspruch 1, dadurch gekennzeichnet, dass das nicht trocknende klebefreudige Harz (b1) ein oder mehrere ionische Gruppen, die mit einem nicht flüchtigen neutralisierenden Mittel neutralisiert worden sind, in einer Menge besitzt, die ausreicht, um das Oligomer oder Polymer wasserlöslich zu machen.

4. Klebelumpen nach Anspruch 1, dadurch gekennzeichnet, dass das nicht trocknende klebefreudige Harz (b2) ein oder mehrere Gruppen besitzt, die nach der Neutralisierung mit einem nicht flüchtigen neutralisierenden Mittel ionische Gruppen in einer Menge bilden, die ausreicht, um das Oligomer oder Polymer wasserlöslich zu machen.

5. Klebelumpen nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die ionischen Gruppen anionische Gruppen sind.

6. Klebelumpen nach einem der Ansprüche 1 bis 4, dadurch gekennzeichnet, dass die ionischen Gruppen kationische Gruppen sind.

7. Klebelumpen nach einem der Ansprüche 1 bis 6, dadurch gekennzeichnet, dass das Gewicht des Klebelumpens 180 - 220 % des Gewichts des Gewebematerials beträgt.

8. Verfahren zur Herstellung Klebelumpens durch Imprägnieren eines Gewebematerials mit einem nicht trocknenden klebefreudigen Harz wie nach einem der Ansprüche 1 bis 7.

5

9. Verfahren zum Säubern eines Klebelumpens nach einem der Ansprüche 1 bis 3 und 5 bis 7, umfassend ein wasserlösliches Oligomer oder Polymer als nicht trocknendes klebefreudiges Harz, dadurch gekennzeichnet, dass der Klebelumpen mit Wasser gewaschen wird, ohne dass oberflächenaktive Mittel zugegeben werden, um das Harz von dem Gewebematerial fast vollständig zu trennen.

10

10. Verfahren zum Säubern eines Klebelumpens nach einem der Ansprüche 4 bis 7, umfassend ein nicht wasserlösliches Oligomer oder Polymer als nicht trocknendes klebefreudiges Harz, dadurch gekennzeichnet, dass der Klebelumpen in Wasser gewaschen wird, ohne Zugabe von oberflächenaktiven Mitteln, um das Harz von dem Gewebematerial fast vollständig zu trennen, wobei das Waschwasser ein nicht flüchtiges neutralisierendes Mittel in einer Menge enthält, die ausreicht, um das Oligomer oder Polymer nach der Neutralisierung dieser Gruppen (b2) wasserlöslich zu machen.

15

20

25

30

35

40

45

50

55